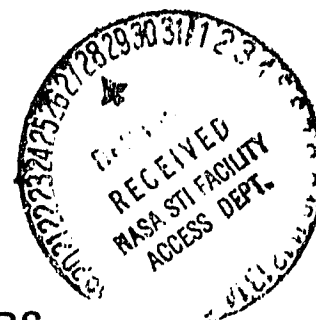


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PLASMA POLYMERIZED HIGH ENERGY DENSITY DIELECTRIC FILMS FOR CAPACITORS

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16. Abstract High energy density polymeric dielectric films were prepared by plasma polymerization of a variety of gaseous monomers. This technique gives thin, reproducible, pinhole-free, conformable, adherent, and insoluble coatings and overcomes the processing problems found in the preparation of thin-films with bulk polymers. Thus, devices can be prepared completely in a vacuum environment. The plasma polymerized films prepared in this study all showed dielectric strengths of greater than 1000 kV/cm and in some cases values of greater than 4000 kV/cm were observed. The dielectric loss of all films was generally less than 1% at frequencies below 10 kHz, but this value increased at higher frequencies. All films were self-healing. The dielectric strength was a function of the polymerization technique, whereas the dielectric constant varied with the structure of the starting material. Because of the thin-films used in this study (thicknesses in the submicron range) surface smoothness of the metal electrodes was found to be critical in obtaining high dielectric strengths. High dielectric strength graft copolymers were also prepared. Plasma polymerized ethane was found to be thermally stable up to 150°C in the presence of air and 250°C in the absence of air. No glass transitions were observed for this material.					
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FOREWORD

This contract was administered by the National Aeronautics and Space Administration, Lewis Research Center. Mr. Stanley Domitz served as the NASA-LeRC project engineer.

The program manager was Dr. Frederick G. Yamagishi, head of the Plasma Chemistry Group of the Device Materials Section, which is headed by Dr. Leroy J. Miller. Professional assistance was provided by Mr. Richard A. Livingston. Technical assistance was provided by Mr. Willis H. Smith, Jr., and Drs. H.P. Gillis and Robert D. Parker served as internal consultants to this program.

Work was performed in the Exploratory Studies Department of Hughes Research Laboratories under the management of Dr. Jan Grinberg.

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SECTION 1

INTRODUCTION

The program described in this report was conducted with the objective of preparing high energy density films specifically for capacitors by the plasma polymerization of a variety of organic starting materials. Polymers have been used successfully as dielectric layers for capacitors in the past. However, these bulk materials must be formed into thin films through various process steps. Further, the reliability of a capacitor is determined by its ability to withstand repeated and lengthy application of electrical stresses and the thermal and mechanical shocks which can be generated by the electrical stresses. The failure of the device is determined by the weakest point in the overall material combination. This is rarely the ultimate limit of the material property. Weak points can usually be traced directly to process problems, either in the film-forming steps or in the device fabrication process. The improvement of materials processing steps (solvent or melt-casting, film rolling and cutting, protection from dirt particles and adsorbed vapors, removal of residual process solvents, etc.) is extremely difficult and expensive. In order to avoid these process problems inherent in bulk polymers, we chose to prepare the polymer films directly, in vacuo, to yield "device precursors." Thus, the device precursors were prepared by depositing the dielectric layer directly onto a metal film. This device precursor was converted into a working capacitor by depositing another metal layer on the the polymer. The devices can be formed in a sandwich configuration simply by repetition of these two deposition steps. The dielectric film prepared in this manner by-passes all problems associated with rolled capacitors using bulk polymers, including the impregnation step with a dielectric fluid to remove air bubbles and voids.

The term "plasma polymerization" generally describes the use of several types of electrical discharge configurations in which molecules (from gaseous monomers) are subjected to energetic electrons in the discharge or plasma. This results in the formation of intermediate free radicals, ions, and other high-energy species derived from the monomer. Interaction among these species ultimately leads to polymerization. There is little discrimination shown in the position of formation for the free radicals in both the monomer and along the growing chains of the polymer. The net result of the propagating step is both a continuing growth of the polymer chains and a developing matrix of crosslink sites. Polymers prepared by this method can vary in structure and molecular weight, depending on the reaction conditions. The polymer can be prepared as an oil, a powder, or a film. To obtain uniform films for a given reactor configuration, the reaction parameters (monomer flow rate, reaction pressure, and discharge power) and, often, substrate surface preparation need to be optimized for each monomer. This optimization will permit very thin, uniform, pinhole-free films to be prepared conveniently. Plasma polymerization affords a unique method for obtaining thin films from monomers that cannot be polymerized by standard chemical techniques. Thus, saturated hydrocarbons, such as ethane, can be polymerized in a glow discharge.

There is ample background that shows that plasma polymerized films are attractive for high energy density dielectrics, particularly for use in capacitors. The technique gives thin, reproducible, pinhole-free, conformable, adherent, and insoluble coatings on essentially any shaped substrate. Films can be deposited on flat substrates for the formation of plane capacitors, or on continuous rolls for wound capacitors. One can envision the coupling of a plasma reactor with a thermal evaporator, allowing the complete fabrication of a device without intermediate exposure of the capacitors to ambient conditions.

The use of polymer thin films as dielectric materials corresponds nearly to the emergence of polymer chemistry as a branch of science. However, it was not until 1960 when Goodman¹ developed a useful preparation technique so that plasma polymerized films could be studied for this purpose. Since that time, several research groups² have investigated the dielectric properties of polymers prepared in a glow discharge.

The principal advantage of plasma polymerized films is that they can be prepared as very thin, pinhole-free, integral coatings. They are known to have a high dielectric strength which, coupled with the small thickness of the film, enhances quadratically the energy capacity of the material.

Bradley and Hammes³ measured the conductivity of plasma polymerized films derived from 40 monomers that varied in structure and polarity. The majority of these films had conductivities in the range of 10^{-16} to 10^{-14} ($\Omega\text{-cm}$)⁻¹ at 150°C. Stuart⁴ reported on the dielectric properties of plasma polymerized styrene which was deposited on a continuous roll of aluminum foil. He found a dielectric loss factor ($\tan \delta$) of 0.001 to 0.003 at 1 kHz and 20°C, with a permittivity of 2.6 to 2.7 between 10^2 and 10^5 Hz. Sar et al.⁵ showed later that the addition of an antioxidant (catechol) to the styrene prior to deposition prevented the formation of polar OH and CO groups in the polymer, and decreased the dielectric loss by a factor of 4-5. Tibbitt et al.⁶ reported similar results with plasma polymerized ethylene-acetylene, ethane-vinyl chloride and tetrafluoroethylene.

Another example of continuous deposition of plasma polymerized films derived from cyclohexane and perfluorocyclobutane was reported by Behn et al.⁷ These films had a dielectric strength of 8×10^6 V/cm. Self-healing wound capacitors of consistently high quality were fabricated from the metalized carrier foils covered with the dielectric film.

Smolinsky and Heiss⁸ demonstrated the reproducibility of the technique for the preparation of capacitors. Out of nearly 200 capacitors, they were able to obtain an 86% yield of working devices. Some shorted capacitors were cleared of defects by subjecting them to a 20 V capacitance discharge.

The approach taken in this project was divided into three technical tasks:

1. Energy Density Enhancement - To deposit plasma polymerized films as the dielectric layer in device precursors, and to determine the minimum thickness (the energy density of a material is inversely proportional to the square of the thickness) needed to completely coat the substrate electrode
2. Plasma Synthesis of New Composite Films - To prepare graft copolymers by plasma polymerization to increase the overall dielectric constant of the composite
3. Polymer Evaluation - To provide dielectric measurements of the devices prepared in the previous tasks.

The results of these tasks are presented and discussed in the next section.

SECTION 2

EXPERIMENTAL

A. PLASMA POLYMERIZED FILMS

Plasma polymerized films were prepared from the following gases:

- Ethane - Matheson Gas Products; Grade: CP
- Ethylene - Matheson Gas Products; Grade: CP
- Tetrafluoroethylene - PCR Research Chemicals; monomer inhibited
- Vinylidene Fluoride - PCR Research Chemicals
- Ethylene Oxide - Matheson Gas Products

These starting materials were used without any further purification.

Three reactors were used to prepare plasma polymerized films. Two reactors were of the bell jar-type, as shown in Figures 1 and 2. A tubular flow reactor, shown in Figure 3, was used for preliminary experiments and for the preparation of the plasma polymerized ethylene oxide films.

A typical film preparation experiment was carried out as follows: The substrate was placed in the appropriate reactor which was pumped to a background pressure of ~60 mTorr, at which time the starting monomer was introduced into the system at ~100 cc/min for at least 15 min. The flow rate was then reduced to a predetermined value, usually ~10 ml/min, and the pressure was adjusted to an optimum value for that particular monomer, usually ~1 Torr, by a throttle valve. Either a Datametrics Baracel or an MKS Baratron pressure regulating system kept the pressure constant throughout the run. Following equilibration of the initial conditions, a plasma was struck using a Tegal P-300 rf generator (13.56 MHz) at 200 to 300 W through an impedance matching network. Since the

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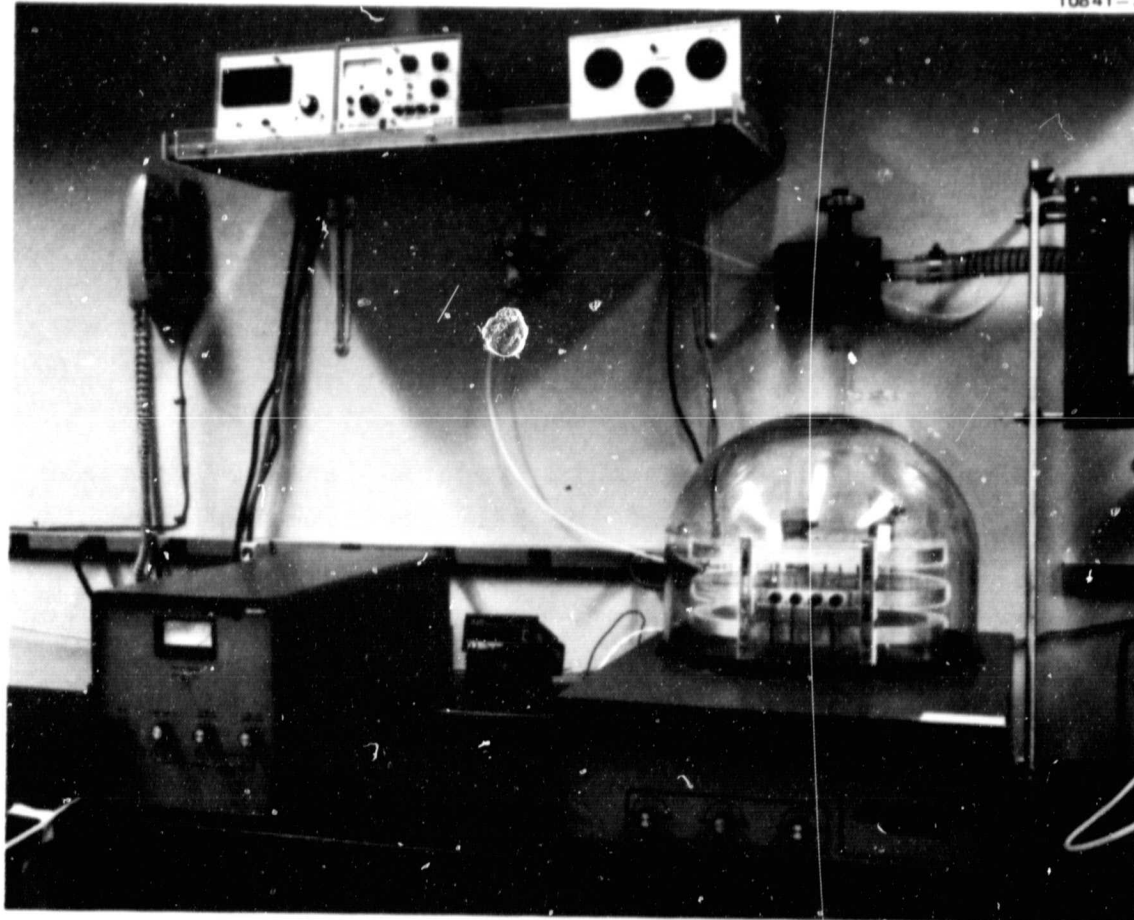


Figure 1. Capacitively coupled bell jar plasma reactor and 300-W rf generator (13.56 MHz).

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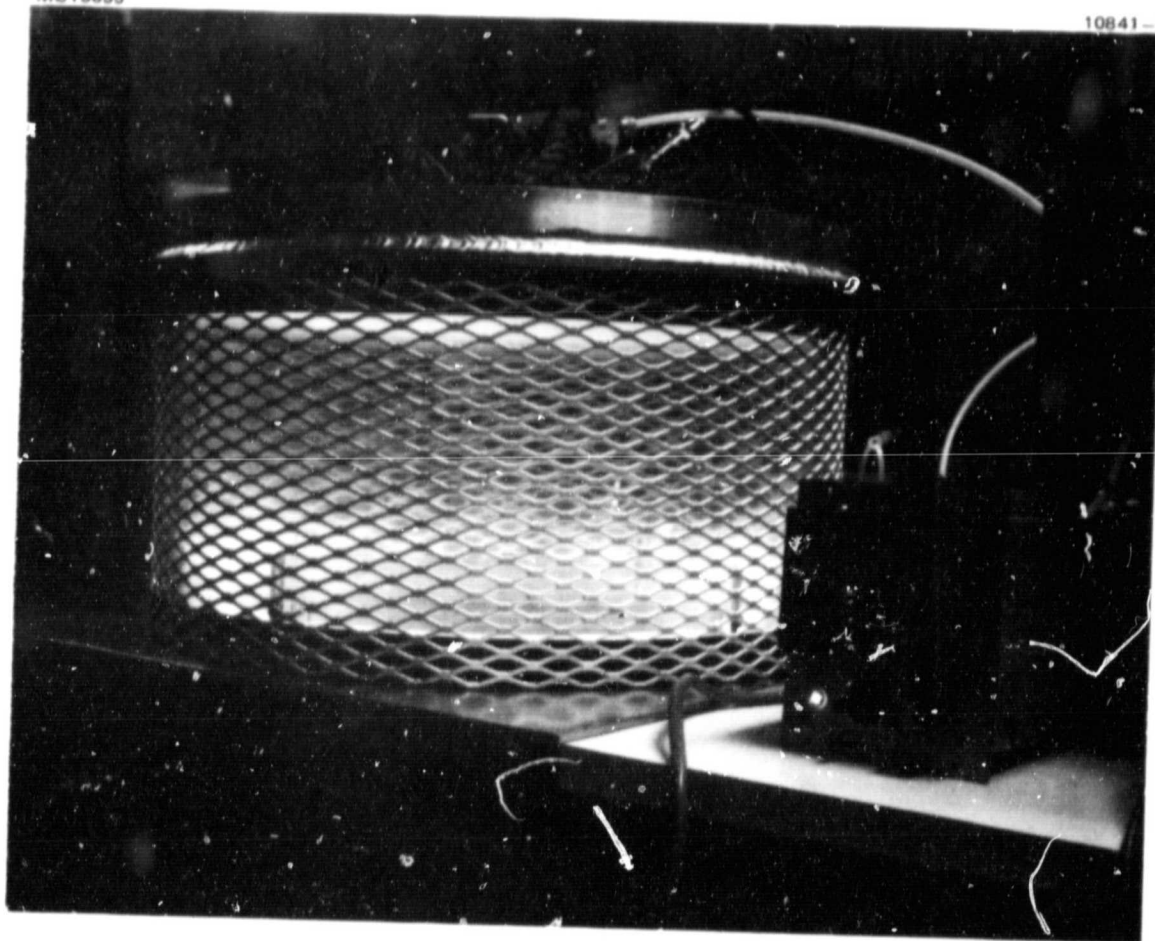


Figure 2. Capacitively coupled plasma reactor with 14-in. diameter electrodes.

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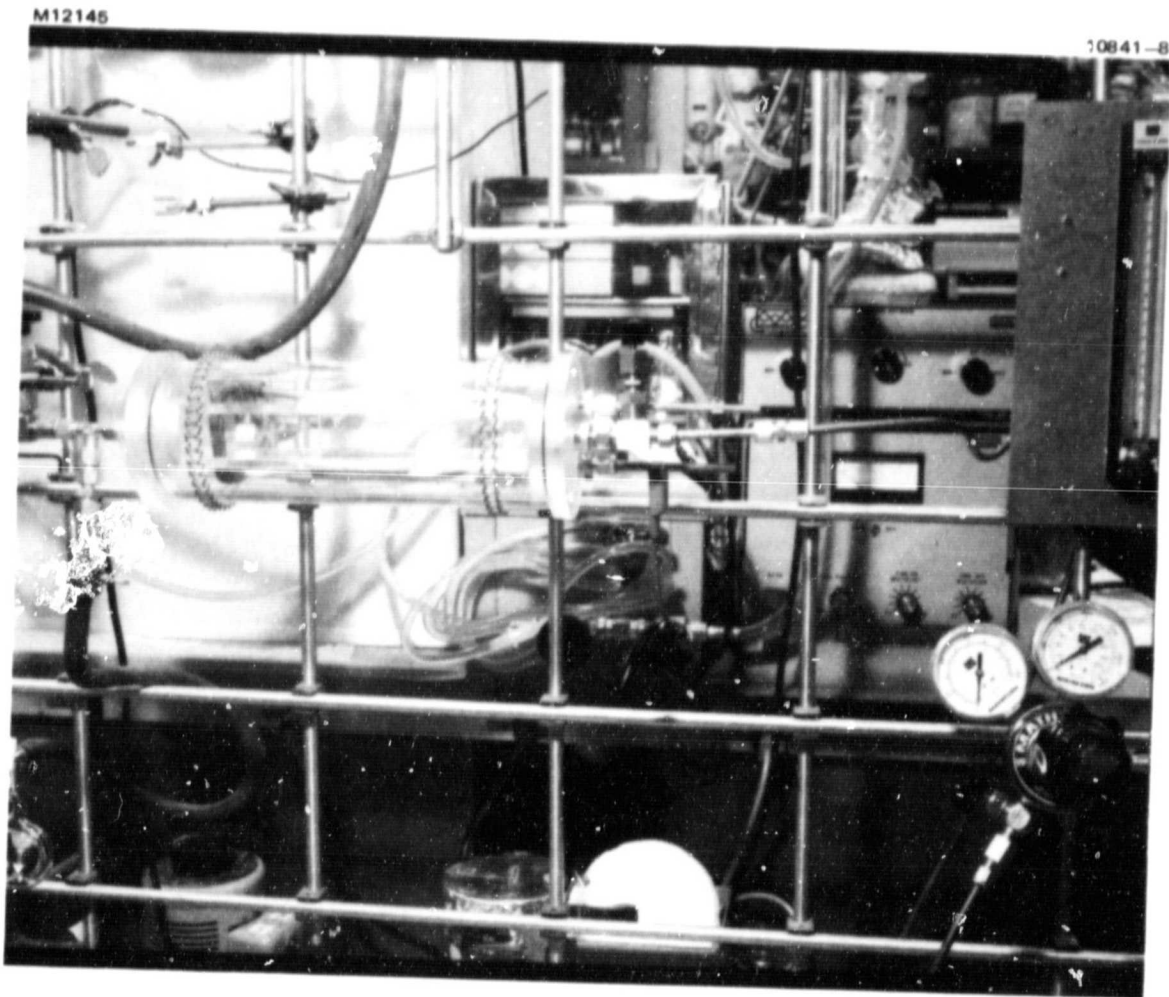


Figure 3. Tubular flow, capacitively coupled plasma reactor.

deposition rate was calibrated under these conditions for a given monomer, desired thicknesses could be obtained by running the experiment for a predetermined time. During the first hour of the experiment, the reaction conditions had to be adjusted slightly due to thermal changes. The final temperature of the system was generally lower than 100°C but rose to 120°C for runs of 20 hr or more. Following the deposition of the plasma polymerized film, the system was evacuated to below 60 mTorr, and in some cases was flushed with ethylene, in the case of hydrocarbon starting materials, or with the corresponding fluorocarbon monomer with fluorocarbon starting materials to quench residual free radicals that were trapped within the polymer matrix. After the reactor cooled to room temperature, or more commonly, after standing overnight, the system was backfilled with air and the substrates removed. At this point, the film was evaluated visually for uniformity, after which electrode pads were deposited on the film forming capacitors, which were then evaluated for their dielectric properties.

B. CAPACITOR DESIGN

The test capacitors used to measure the dielectric properties of the various plasma polymerized films were of the sandwich, planar configuration. Most of the test devices were prepared using glass microscope slides as the substrate. Aluminum (approximately 4000 Å) was thermally evaporated on the microscope slide, except for a strip along one long edge. The plasma polymerized film was deposited over the entire surface, after which aluminum pads (approximately 2000 Å) of varying areas were deposited on the polymer film. Adhesion of the aluminum to the polymer was generally not a problem with the hydrocarbon films. Initially, however, adhesion of the aluminum to the fluorocarbon films was a problem, which eventually lessened as the quality of the fluorocarbon film increased. Capacitors of this type are shown in Figure 4. We also prepared test devices using a smooth silicon wafer as the

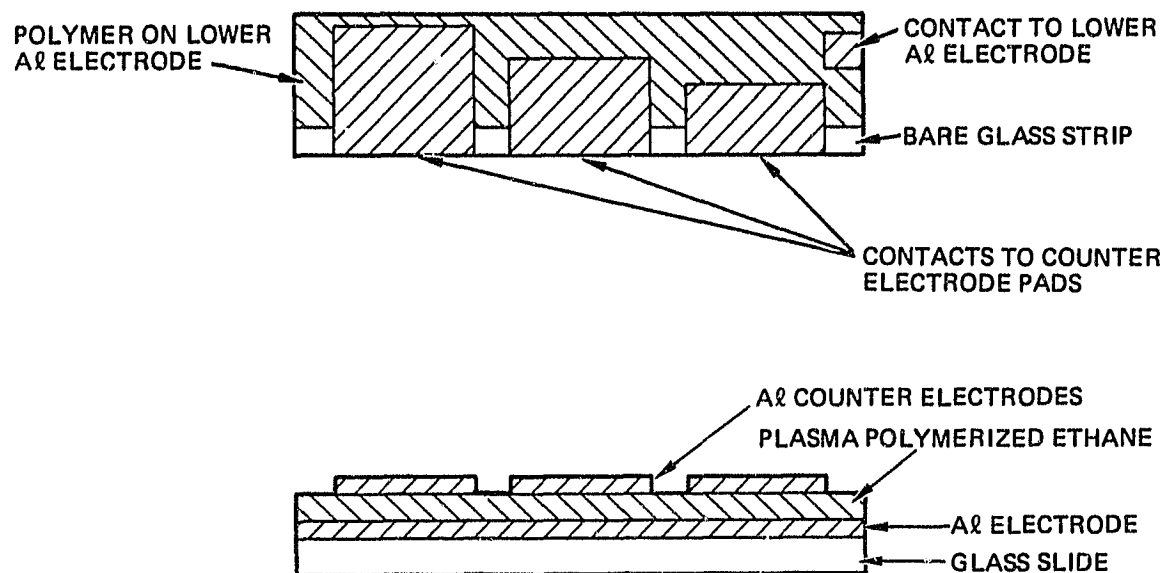


Figure 4. Test capacitors on aluminized glass slides with the plasma polymerized film sandwiched between evaporated aluminum electrodes.

substrate. The surface roughness of the aluminized microscope slide was of the same magnitude as the desired thickness of some of the plasma polymerized films; thus a smoother surface was required for very thin dielectric layers. A thin oxide layer (approximately 4000 Å) was thermally grown on the polished side on an undoped Si wafer. Aluminum was then deposited, followed by polymer film deposition and aluminum pad deposition. In both cases, contact to the bottom electrode was accomplished by carefully scraping away the plasma polymerized film.

C. DIELECTRIC PROPERTY MEASUREMENTS

Electrical contact to the test capacitors was made using very small alligator clips which had been modified by filling their jaws with solder to make a rounded, smooth bump. This avoided damage to the thin aluminum film. Capacitance and dissipation factor measurements were made with a Hewlett-Packard 4274A multi-frequency LCR meter at 100 Hz, 1 KHz, 10 KHz, and 100 KHz. Breakdown voltage measurements were then taken. The schematic of the breakdown voltage circuit, which uses an oscilloscope and a dc power supply, is shown in Figure 5. This system takes advantage of the 1 MΩ input resistance of the scope to function as an electrometer. Currents of less than 50 nA were readily discernable.

During the breakdown voltage measurements a clearing effect was observed in most of the devices. That is, as the voltage was increased, at some point the capacitor would momentarily break down. From that time on, it would not break down at that voltage or any lower voltage. The breakdown process appears to blast away the aluminum and plasma film from the areas of the weak point. An example of this clearing effect is shown in Figure 6. During these discharges, a small pinpoint flash of light was usually visible somewhere on the sample. The breakdown voltage was recorded as the highest voltage that the film could withstand before finally shorting.

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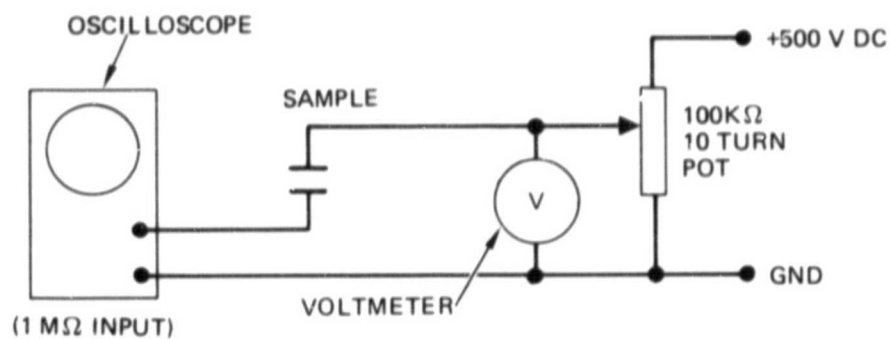


Figure 5. Initial schematic of the breakdown voltage measurement circuit which uses an oscilloscope and a dc power supply.

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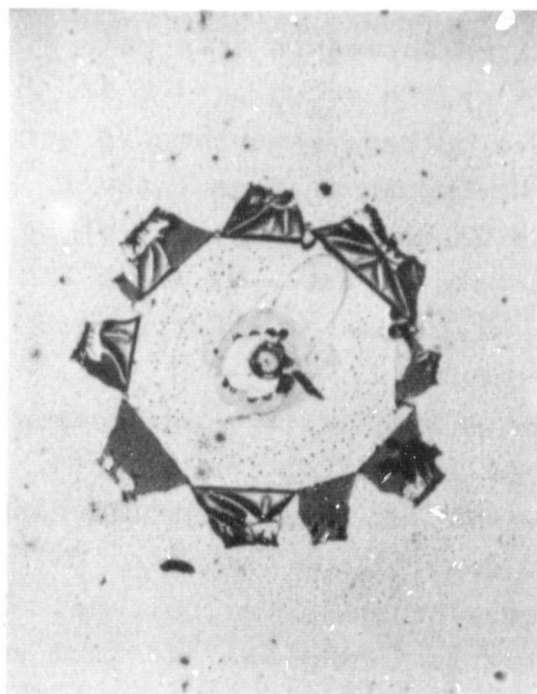


Figure 6. Cleared area in a test capacitor using plasma polymerized ethane.

The dielectric constant, k , was calculated from the capacitance measurements using the formula

$$k = \frac{Cd}{8.85 \times 10^{-14} A} ,$$

where C is the capacitance (μF), d is the thickness (μm), and A is the area (mm^2) of the device.

Two revisions were incorporated into the circuitry for measuring the breakdown voltages. Clearing of individual capacitors was accomplished by discharging a $0.091 \mu F$ mica capacitor, which had been charged to 10 V into each capacitor as it was tested, with the positive terminal on the upper electrode. This modification is shown in Figure 7. During the dielectric strength tests, this capacitor was left in the circuit to facilitate the clearing of the capacitors in each device precursor. The second modification is shown in the schematic in Figure 8. The basic change was the introduction of a transformer to couple to the oscilloscope which was used as a failure detector. Using the input circuit of the oscilloscope directly places a rather severe strain on the input when a film fails at a high voltage. The transformer transfers the current pulse in $R_1 + R_2 + R_3$ into a voltage spike. A continuous breakdown or a high leakage in the film will be detected by a constant deflection on the ammeter in series with the $1 M\Omega$ resistor string.

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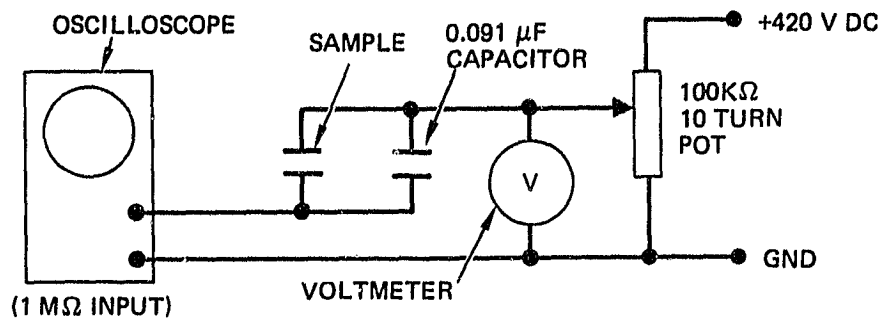
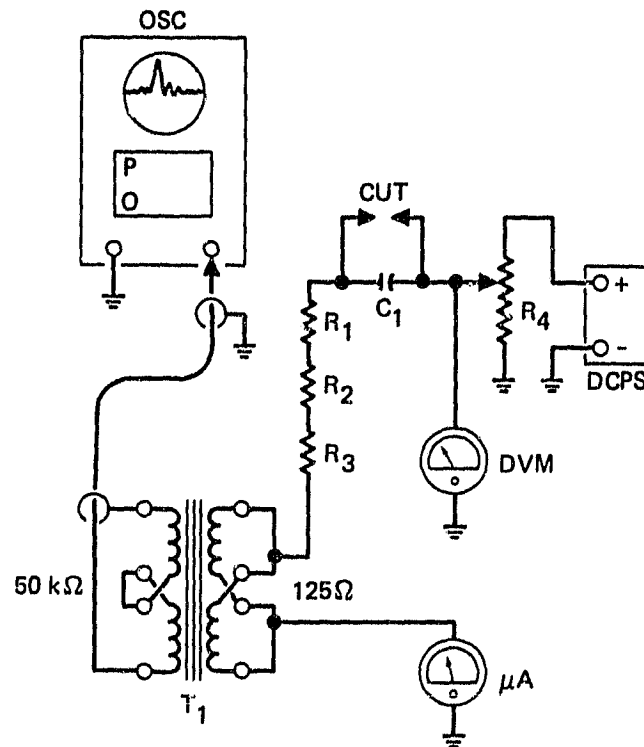


Figure 7. Schematic of the first modification to the breakdown voltage measurement circuit, including a 0.091 μF capacitor used to facilitate the clearing of the test capacitor.



OSC TEK 547 OSCILLOSCOPE

P TEK 1A1 PLUG IN

T₁ UTC A10 LINE TO GRID TRANSFORMER CONNECTED 125Ω TO 50K

μA WESTON 931 μAMP METER

R₁ + R₂ + R₃ TOTAL RESISTANCE 1 MΩ

C₁ 0.091 μF DIPPED MICA CAP

CUT CAPACITOR UNDER TEST

DVM FLUKE 8502A DIGITAL MULTIMETER

R₄ 0 - 100KΩ 10 TURN POT

DCPS KEPKO LABS MODEL 815 VARIABLE VOLTAGE DC POWER SUPPLY

Figure 8. Schematic of the second modification to the breakdown voltage measurement circuit, which uses a transformer to couple to the oscilloscope.

SECTION 3

TECHNICAL DISCUSSION

The program on plasma polymerized high energy density dielectric films for capacitors was divided into three technical tasks and one reporting task. This section discusses, task by task, the problems and solutions encountered during the extent of the contract. Conclusions that can be drawn from the results of these tasks will be discussed in the following section.

A. TASK 1. ENERGY DENSITY ENHANCEMENT

- Deposit films, which will achieve an energy density goal of 5 J/gram or greater, by plasma polymerization from monomers including, but not necessarily limited to, ethane, ethylene, tetrafluoroethylene, and ethylene oxide.
- Determine minimum thickness necessary to completely coat the substrate, such as thermally evaporated aluminum on a glass slide, to eliminate pinholes.

The energy density, k_c (energy per unit mass) for a dielectric material can be expressed as:

$$k_c \equiv \frac{E}{m} = \frac{\kappa \epsilon_0}{2\rho} \left(\frac{V}{d}\right)^2 ,$$

where E is the energy stored, m is the mass, κ is the relative permittivity of the dielectric, ϵ_0 is the permittivity of free space (8.85×10^{-14} F/cm), ρ is the density of the dielectric (g/cm^3), V is the breakdown voltage, and d is the thickness of the dielectric film. The term k_c is thus given in units of J/g. Hence, for a given device, the energy density stored increases with voltage across the leads in a quadratic fashion, with the limit being determined in principle by the ultimate breakdown voltage of the dielectric. Furthermore, the energy storage density also depends quadratically on the reciprocal of the film thickness.

The method of plasma polymerization offers advantages over bulk polymerization through improvements in the quality of the film. The polymer can be deposited as a pinhole-free film directly, thereby eliminating dangerous material processing steps (film casting, rolling, cutting, storing) which would lead to film damage and ultimate failure of the dielectric layer.

We prepared films by plasma polymerization from a variety of polar and nonpolar monomers. Based on previous results from both the literature and from our laboratory, a high voltage breakdown was expected and achieved. Furthermore, plasma polymerization is the method of choice for the preparation of very thin, uniform, and pinhole-free films. The quadratic relation between breakdown voltage and thickness was exploited to enhance the energy density of the resulting dielectric films.

1. Plasma Polymerized Ethane

The largest effort to prepare films as high energy dielectrics for capacitors was directed toward the development of plasma polymerized ethane (PPE) for this purpose. The polymerization conditions were optimized in the bell jar reactor after preparing films under three different reaction conditions:

<u>No.</u>	<u>Flow Rate (ml/min @ STP)</u>	<u>Pressure (Torr)</u>	<u>RF Power (Watts)</u>
1	10	1.00	200
2	49	0.9	200
3	10	1.5	200

Method 1 proved to be the optimum condition to obtain highly uniform, reproducible films. The film obtained from Method 2 contained a high concentration of defects, presumably pinholes, which led to almost immediate shorting of the resulting capacitor with the application of voltage. Method 3 resulted in a deposition rate of nearly 2 times that of Method 1, but the film was much more yellow (presumably from the greater inclusion of carbon-carbon double bonds in the polymer) and was non-uniform around the edges. Similar experiments were done with the large reactor to determine the optimum reaction conditions. Once these conditions were defined, they were used throughout the study.

Films of both PPE and plasma polymerized ethylene, PPEE, prepared early in this program showed hillocks that were observable by optical microscopy. Scanning electron micrographs (see Figure 9) showed that these hillocks were between 0.8 and 4 μm in diameter and that they did not appear to be as high as they were wide. These hillocks or embedded particles may have been due to defects, e.g., bumps on the aluminum film, or to the oligomerization of the monomer in the gas phase, which would lead to the deposition of particles. However, they did not appear to cause a major problem with device failure; i.e., shorting did not occur specifically at the hillock sites, although they may have played a role in the ultimate dielectric strength of the material. Since these hillocks did not adversely effect dielectric measurements, their presence was not followed throughout this study. However, the dielectric strength of the PPE films increased as more uniform films were prepared during the course of this program.

Essentially all of the samples studied were less than 2- μm thick and dielectric strengths of greater than 1000 kV/cm were commonly observed. On the glass slides, the minimum thickness that was found to completely cover surface defects by PPE was 0.27 μm . However, this thickness was found to give non-reproducible results; several of the devices were shorted.



(a) PLASMA POLYMERIZED ETHANE



(b) PLASMA POLYMERIZED ETHYLENE

Figure 9. Scanning electron micrographs of some plasma polymerized ethane and ethylene films.

Thicknesses of between 0.6 and 0.8 μm did yield reproducible results with dielectric strengths of over 4000 kV/cm. High, reproducible dielectric strength values were obtained with a 0.28- μm -thick PPE film by using the smooth Si substrates. These results amplify the need for considering all aspects in fabricating planar capacitors, rather than just the dielectric film. This is particularly true when trying to increase the dielectric strength by reducing the thickness of the dielectric film.

2. Plasma Polymerized Ethylene

Conditions were established to give uniform plasma polymerized ethylene (PPEE) films with a deposition rate of 0.45 $\mu\text{m/hr}$ in the large reactor. As with PPE, high dielectric strengths were obtained. Commonly, values of greater than 2000 kV/cm were observed. Capacitors using PPEE thicknesses of 0.1 and 0.05 μm were prepared. Under the reaction conditions used, and with this particular set of aluminum electrodes on glass slides, these thicknesses of PPEE were not adequate to completely coat the defects on the surface. Consequently, all of the devices were shorted and they could not be cleared with applied voltage. Therefore, no dielectric data could be obtained. However, a 0.46- μm -thick PPEE film yielded a working capacitor with a dielectric strength of 2170 kV/cm.

3. Plasma Polymerized Vinylidene Fluoride

A considerable effort went into the deposition of high quality plasma polymerized vinylidene fluoride (PPVF_2) in both the bell jar and large reactors. Several characterization runs had to be carried out to obtain reaction conditions that would yield a film rather than a powder. A total of 19 experiments, which varied the reaction pressure, flow rate, and input power, were carried out until reproducible films could be obtained. We found that the monomer would spontaneously polymerize in the reactor, even before a plasma was struck. We adjusted our technique to minimize this problem by thoroughly evacuating the

system before the introduction of the vinylidene fluoride and then striking the plasma as soon as the system equilibrated after the introduction of the monomer gas. Using this procedure, rather than flushing the system with monomer for several minutes, tremendously minimized the problem, and consequently, the quality of the films increased with successive runs.

Another problem that had to be overcome involved the adhesion of PPVF₂ to the aluminized glass slides. It appeared that this polymer had a low sticking coefficient and therefore even films that were removed from the reactor which appeared to be of high quality readily crazed with little or no provocation. Cleaning the surface, however, with Micro Cleaner followed by thorough rinsing, and accompanied by an oxygen plasma scrub prior to the deposition of the PPVF₂ greatly increased the adherence of the film to the substrate.

4. Plasma Polymerized Tetrafluoroethylene

Reaction conditions in the bell jar reactor were obtained that appeared to yield highly uniform plasma polymerized tetrafluoroethylene (PPTFE) films. However, our initial capacitors showed significant conduction. On the large pad, a current of about a microamp was obtained at 30 V. This resulted in little reproducibility in the capacitance measurements and therefore in the dielectric constant calculations. Adjustment of the reaction conditions again gave high quality films, but the capacitors prepared from film also showed a nonlinear conductivity. At some voltage, the leakage current would begin to increase rapidly as the voltage applied was increased. However, these devices could be cleared and dielectric data could be obtained.

Films of PPTFE prepared in the large reactor did not show this conduction and dielectric data could be readily obtained. Dielectric strengths of more than 1000 kV/cm up to 2400 kV/cm were obtained with these films. In some cases the entire device was overcoated with an additional layer of PPTFE to prevent

flashover or the development of high fields near the edges of the devices. No dramatic differences or inconsistencies in the dielectric strength were observed between the overcoated and non-overcoated samples. Thus, it appears that flashover is not a problem in our measurement technique and that dielectric breakdown is not dominated by decomposition at the edges of the top electrode pads.

A film thickness of about 0.5 μm was adequate to cover surface defects on aluminized glass slides and reproducible data could be obtained without having to force clearing events to occur.

5. Plasma Polymerized Ethylene Oxide

Our initial attempts to prepare plasma polymerized ethylene oxide (PPEO) films were hampered by the fact that the ethylene oxide reacted with the Viton o-ring seals in the rotameters (flow rate tubes). Because of this reaction the flow into the reactor was non-uniform and, in fact, the flow actually stopped after about 30 min. This was not an adequate time, for the reaction conditions used, to yield a film thick enough to adequately cover all surface defects. The Viton seals were replaced with Teflon seals which eliminated the problem. It was found that a 0.45- μm -thick film of PPEO yielded working capacitors with dielectric strengths approaching 2000 kV/cm.

B. TASK 2. PLASMA SYNTHESIS OF NEW COMPOSITE FILMS

- Prepare by plasma synthesis graft copolymers comprising layers of nonpolar polymers derived from monomers including, but not necessarily limited to, ethane, ethylene, or cyclohexane, and polar or polarizable polymers derived from monomers, including ethylene oxide and vinylidene fluoride, to increase the dielectric constant of the composite, with a goal of greater than or equal to 12.
- Provide at least 10 capacitor precursor test devices of each plasma polymerized film or graft copolymer for evaluation.

The impetus behind this task evolved from the studies⁹ of polystyrene (PS)-polyethylene oxide (PEO) block copolymers which showed that unusually high dielectric constants could be achieved in phase separated systems. In this case the system is composed of two dissimilar polymers, one highly polar and semi-crystalline (PEO), the other, nonpolar and amorphous (PS). The dielectric behavior of this system was found to be highly dependent on the morphology, which was determined by the composition and solvent used to cast the films. For a PS composition of 50 wt%, the dielectric constant increased abruptly at 64°C, or near the melting point of PEO (65°C), to a value of 25 at 1 kHz in films cast from chloroform, a solvent in which both moieties were soluble. Increasing the concentration of PS in the block copolymer, or casting from a solvent that preferentially solubilizes PS, resulted in a lowering of the dielectric constant and a broadening of the temperature effect. Although no mechanism for these observations was presented, there appears to be a correlation between the morphology, concentration, and crystallinity of the PEO block. The authors point out that the increase in dielectric constant with increasing temperature may be due to the softening of the matrix and coalescence and gross phase separation of PS and PEO, allowing for large, continuous sections of PEO within the amorphous polymer matrix. In fact, when the PEO units are widely dispersed (low concentration) or embedded in a PS matrix (casting solvent history), there is little or no interaction between PEO blocks, and consequently, no increase in the dielectric constant was observed.

We prepared, by plasma synthesis, graft copolymers comprising layers of nonpolar polymers derived from the monomer ethane, and polar or polarizable polymers derived from monomers such as vinylidene fluoride, and tetrafluoroethylene. The residual free radicals of the first deposited layer interacted with the active species involved in the formation of the second

layer to form discrete carbon-carbon bonds. This formed a system with a well defined nonpolar-polar interface, and each layer of the system could intramolecularly interact continuously. Based on the results obtained in the block copolymer case discussed above, it was expected that the dielectric constants of these novel plasma polymerized graft copolymers would be increased substantially over the dielectric constants of the individual layers. We expected to achieve a value of ~ 12 for the dielectric constant. It was further expected that there would be a concomitant increase in the dielectric loss, which must be taken into account in the preparation of practical devices. The increase in the dielectric constant, coupled with the high voltage breakdown values obtained in the films prepared in Task 1, was expected to provide a dielectric material with an energy density approaching 5 J/g.

Graft copolymer structures were prepared by allowing each plasma polymerized film to be deposited under conditions that were found to be optimum for that particular monomer. After the first film was deposited, the system was pumped to a pressure below 100 mTorr (typically 70 mTorr) and the monomer used for the second layer was admitted into the system, equilibrated to the proper conditions, after which the plasma was struck. Each layer was deposited for a predetermined time to obtain a desired thickness.

Our first attempts to prepare graft copolymers by plasma synthesis involved the structures PPE on PPVF₂, PPE on PPTFE, and PPTFE on PPE. The total thickness of these composites was found to be less than calculated, as shown below:

SAMPLE	POLYMER	CALCULATED THICKNESS, μm	TOTAL MEASURED THICKNESS, μm
PPE on PPVF ₂	PPE	1.1	1.27
	PPVF ₂	0.43	
PPTFE on PPE	PPE	0.55	1.00
	PPTFE	0.65	
PPE on PPTFE	PPE	0.55	0.75
	PPTFE	0.65	

The reason for this discrepancy is not known. However, it is possible that the second layer may have sputtered the first layer prior to the deposition of the former. Also, the second layer was deposited soon after the deposition of the first layer was completed. Consequently, the substrate was still relatively warm. The deposition rate of the plasma polymerized films is known to be enhanced when the electrodes are cooled, and our deposition rates are determined for reactions on substrates at room temperature, which are gradually heated during the course of the deposition. Yet despite this rationale, the next set of graft copolymers corresponded to the calculated thickness of each individual layer, as shown below.

SAMPLE	POLYMER	CALCULATED THICKNESS, μm	TOTAL MEASURED THICKNESS, μm
PPVF ₂ on PPE	PPVF ₂	0.43	0.68
	PPE	0.27	
PPE on PPTFE on PPE	PPE	0.27	1.29
	PPTFE	0.65	
	PPE	0.41	

The discrepancy in the first set of graft copolymers remains a mystery. Because of the difficulty in preparing uniform films of PPEO, coupled with the results of the graft copolymers prepared to this point (see below), we felt that the attainment of enhanced dielectric constants by this approach was improbable. Consequently, we concentrated our efforts more on increasing the energy density of single layer films.

Since the dielectric materials prepared in this program were deposited as thin films only a few micrometers thick, it was not feasible or applicable to provide gram quantities of the polymer as stipulated in the Statement of Work of the Request for Proposal. Instead, we prepared 10 capacitor precursor test devices of each plasma polymerized film for evaluation. These devices were fabricated by depositing aluminum on glass slides on which the plasma polymerized film was deposited, followed by the deposition of aluminum counter electrode pads. These devices were delivered prior to the submission of this report.

C. TASK 3. POLYMER EVALUATION

- Measure the following specific properties of the plasma polymerized films prepared in Tasks 1 and 2:
 - Density
 - Glass transition temperature (T_g)
 - Dielectric strength
 - Dielectric constant up to T_g
 - Dissipation factor up to T_g and 1 MHz.

The plasma polymerized high energy density dielectric films prepared in Tasks 1 and 2 were evaluated for their electrical and physical properties. The density of the plasma polymerized films was determined by suspending the polymer in solvents of known density. The electrical properties were measured on plane test capacitors. For capacitance and dissipation measurements, the sample was used as prepared. For dielectric breakdown strength, samples were either used as prepared, or an additional

layer of polymer was deposited over the entire device to prevent flashover or the development of high fields around the edges of the device. The electrical measurements were done in conformance with ASTM D-149 for the breakdown tests and ASTM D-150 for the dielectric constant and dissipation factor.

1. Dielectric Data

The dielectric data for the various plasma polymerized films are summarized in the following Tables 1 through 6. High dielectric strengths, of greater than 1000 kV/cm were observed with all materials, indicating that this property is a function of the plasma polymerization technique rather than being an inherent property of each particular starting material. In general, the higher values of the dielectric strength were observed in the devices using thin dielectric films. The capacitance does not appear to be a function of frequency. However, as is commonly seen in polymers, the dielectric loss (dissipation factor) is indeed highly influenced by frequency. The dissipation factor was generally much below 1% at frequencies below 10 kHz, but increased rapidly at frequencies above 10kHz.

The dielectric constants, however, are a function of the structure of the starting materials, and consequently, of the resulting plasma polymerized film, as shown below:

POLYMER	MEAN DIELECTRIC CONSTANT, k	STANDARD DEVIATION
PPE	2.50	0.25
PPEE	2.75	0.26
PPVF ₂	3.16	0.41
PPTFE	2.39	0.16
PPEO	3.03	0.27

Table 1. Dielectric Data on Plasma Polymerized Ethane

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)				k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)	Comments
		100 Hz	1 kHz	10 kHz	100 kHz				
0.6	348	13.38nF 0.20%	13.34nF 0.28%	13.28nF 0.42%	13.20nF 1.67%	2.60	-	-	13.38nF/12.60% @ 1 MHz
	226	8.48 0.20	8.45 0.24	8.41 0.48	8.36 2.21	2.53	-	-	8.28nF/17.97% @ 1 MHz
	125	4.62 0.20	4.60 0.26	4.58 0.36	4.57 0.91	2.50	1780		4.54nF/4.87% @ 1 MHz
	152	5.38 0.18	5.36 0.27	5.04 0.37	5.02 0.98	2.39	1330		5.03nF/6.23% @ 1 MHz; overcoated with PPE
1.18	385	6.66 0.15	6.65 0.19	6.63 0.34	6.60 1.52	2.30	1250		6.60nF/2.30% @ 1 MHz
	209	4.13 0.15	4.12 0.18	4.11 0.26	4.09 0.73	2.63	1090		4.08nF/4.30% @ 1 MHz
1.18	123	2.41 0.20	2.40 0.20	2.39 0.33	2.38 1.41	2.60	1310		2.37nF/69.0% @ 1 MHz
	198	3.83 0.17	3.82 0.19	3.81 0.79	3.79 0.65	2.57	1530		3.79nF/3.16% @ 1 MHz; overcoated with PPE
	93	1.86 0.21	1.85 0.24	1.84 0.42	1.84 1.13	2.65	1570		1.83nF/3.25% @ 1 MHz; overcoated with PPE
1.12	329	6.13 0.15	6.12 0.16	6.09 0.39	6.07 2.37	2.34	595		Overcoated with PPE
1.12	217	4.00 0.14	3.99 0.18	3.98 0.25	3.96 1.06	2.32	696		Overcoated with PPE
1.12	111	2.09 0.19	2.09 0.23	2.08 0.29	2.07 0.85	2.38	921		Overcoated with PPE
0.77	337	9.40 0.06	9.38 0.09	9.37 0.19	9.36 1.03	2.42	1920		
	215	6.00 0.05	6.00 0.09	5.99 0.14	5.98 0.54	2.43	2210		
0.86	109	2.99 0.08	2.98 0.10	2.98 0.14	2.97 0.46	2.38	2360		
	197	5.78 0.07	5.78 0.12	5.77 0.28	5.75 1.76	2.85	3640		Devices on a Si wafer
0.28	136	4.01 0.14	4.00 0.18	3.99 0.29	3.98 1.06	2.86	4070		Devices on a Si wafer
	78	2.29 0.12	2.29 0.14	2.28 0.19	2.28 0.63	2.84	2730		Devices on a Si wafer
0.64	198	19.62 0.60	19.41 0.71	19.28 2.20	19.04 16.89	3.1	1214		
	134	12.56 0.42	12.47 0.53	12.39 1.38	12.16 8.75	2.9	3607	1.86	
	71	7.71 0.46	7.64 0.52	7.59 0.95	7.49 0.44	3.4	2680		
	375	13.34 0.41	13.25 0.52	13.15 1.16	12.93 5.95	2.6	-		
	233	8.33 0.42	8.28 0.52	8.21 0.96	8.08 3.68	2.6	3125		
	137	4.98 0.40	4.95 0.49	4.91 0.78	4.85 2.38	2.6	4063	2.11	Unsteady Pressure, no ethylene quench

Table 1. Continued

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)				k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)	Comments
		100 Hz	1 kHz	10 kHz	100 kHz				
1.08	356	7.70nF 0.31%	7.66nF 0.39%	7.61nF 0.70%	7.53nF 2.42%	2.6	-		
	234	4.89 0.28	4.87 0.36	4.84 0.58	4.90 1.68	2.5	-		
	115	2.51 0.32	2.49 0.41	2.48 0.62	2.45 1.43	2.6	2778	0.99	
0.40	367	21.53 0.41	21.39 0.49	21.23 0.85	20.99 3.02	2.6	-		
	236	13.45 0.38	13.18 0.46	13.08 0.71	12.93 1.80	2.5	-		
	113	7.87 0.44	7.81 0.52	7.75 0.74	7.65 1.53	2.7	3375	1.51	No ethylene quench
1.1	362	6.45 0.06	6.44 0.11	6.43 0.18	6.42 0.67	2.2	-		
	256	4.58 0.04	4.58 0.10	4.57 0.14	4.56 0.50	2.2	2273		
	130	2.45 0.05	2.44 0.10	2.44 0.14	2.43 0.34	2.3	2727	0.73	
0.27	369	30.19 0.32	30.02 0.48	29.83 1.57	29.54 7.32	2.5	-		
	234	19.13 0.34	19.02 0.44	18.90 1.01	18.71 5.28	2.5	-		
	124	10.10 0.32	10.04 0.40	9.98 0.74	9.88 3.14	2.5	1852	0.42	
0.60	232	7.37 -	7.26 0.26	7.24 0.56	7.21 2.96	2.12	2500		
	142	4.37 0.26	4.34 0.26	4.32 0.46	4.31 1.76	2.07	2833	0.82	
1.80	342	4.27 -	4.21 0.26	4.19 0.36	4.17 1.46	2.50	1056		
	243	2.99 -	2.95 0.26	2.94 0.28	2.93 1.06	2.47	1278	0.20	
	136	1.69 -	1.62 0.28	1.62 0.28	1.60 0.76	2.42	1167		
11.0	129	0.366 -	0.256 -	0.251 0.26	0.294 0.46	2.47	>517		Breakdown not observed at maximum voltage
2.7	375	3.02 0.2	3.01 0.4	3.01 0.5	-	2.44	1960+		
	219	1.79 0.2	1.78 0.2	1.79 0.2	-	2.49	1960+	0.46	
	112	0.90 0.1	0.90 0.3	0.90 0.3	-	2.45	1960+		
1.2	346	5.94 0.2	5.93 0.3	5.92 0.3	-	2.32			
	243	4.18 0.2	4.18 0.3	4.16 0.3	-	2.32			
	124	2.17 0.3	2.17 0.4	2.16 0.4	-	2.36			
1.77	233	2.57 0.3	2.57 0.13	2.56 0.18	2.56 0.45	2.2	1980	0.42	

Table 2. Dielectric Data on Plasma Polymerized Ethylene

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)					k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)
		100 Hz	1 kHz	10 kHz	100 kHz				
1.32	419	- nF - %	8.01nF 0.7 %	7.91nF 1.5%	7.74nF 5.9%		2.85	1980	
	266	-	5.18 0.7	5.12 1.2	5.02 3.1		2.90	2270	
	157	-	3.30 0.7	3.27 0.7	3.20 1.1		3.14	2730	
0.46	222	-	12.36 0.6	12.25 0.9	12.01 2.2		2.89	-	
	113	6.08 0.3	6.05 0.6	5.99 0.9	5.91 1.7		2.78	2170	
0.1			ALL DEVICES WERE SHORTED						
0.05			ALL DEVICES WERE SHORTED						
2.25	327	3.14 0.3	3.14 0.17	3.13 0.28	3.11 0.75		2.42	-	
	229	2.21 0.3	2.21 0.16	2.19 0.26	2.19 0.71		2.43	2220+	0.60
	117	1.18 0.5	1.18 0.27	1.18 0.34	1.17 0.54		2.55		

Table 3. Dielectric Data for Plasma Polymerized Vinylidene Fluoride

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)					k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)
		Capacitance (nF) and Dissipation Factor (%)							
		100 Hz	1 kHz	10 kHz	100 kHz				
0.57	353	6.35nF 0.9%	18.37nF 0.7%	18.18nF 1.0%	17.95nF 2.4%	3.33	1110		
	233	-	11.99 0.7	11.86 1.6	11.66 2.0	3.29	1130		
	111	6.31 0.1	5.81 0.7	5.75 0.9	5.66 1.6	3.35	1180		
0.13	222	61.5 2.1	60.2 1.5	59.1 2.1	-	3.98	1690		
0.20	242	35.8 1.2	35.4 1.1	34.8 1.5	-	-	-		
0.35	137	18.0 1.1	17.9 1.1	17.4 1.3	-	-	1250		
	251	19.2 2.2	18.78 1.5	-	-	2.56	3030		
	111	8.0 1.6	7.83 1.4	-	-	2.79	2230		
1.2	228	5.45 0.5	5.40 0.6	5.35 1.0	-	3.21	3180		
	115	2.57 0.5	2.55 0.6	2.52 0.9	-	3.01	3640		

Table 4. Dielectric Data for Plasma Polymerized Tetrafluoroethylene

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)				k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)	Comments
		100 Hz	1 kHz	10 kHz	100 kHz				
0.52	335	14.81nF 0.25%	14.76nF 0.47%	14.69nF 0.64%	14.60nF 4.12%	2.59	1270		14.74nF/36.24% @ 1 MHz
	213	9.24 0.23	9.20 0.26	9.16 0.33	9.12 1.06	2.54	1920		9.12nF/6.77% @ 1 MHz
	123	5.36 0.25	5.33 0.33	5.30 0.35	5.27 0.81	2.55	1580		5.25nF/3.64% @ 1 MHz
	343	13.97 0.24	13.91 0.27	13.85 0.42	13.78 1.93	2.38	2060		13.99nF/15.84% @ 1 MHz; overcoated with PTFE
1.26	217	9.21 0.25	9.18 0.27	9.14 0.57	9.08 3.59	2.48	2400		9.13nF/32.14% @ 1 MHz; overcoated with PTFE
	121	5.01 0.26	4.99 0.28	4.97 0.71	4.94 4.60	2.42	2270		4.93nF/32.3% @ 1 MHz; overcoated with PTFE
1.26	385	5.66 0.19	5.64 0.21	5.62 0.28	5.60 0.89	2.40	1510		5.60nF/5.80% @ 1 MHz
	108	1.85 0.25	1.85 0.26	1.84 0.31	1.83 0.84	2.44	1670		1.82nF/4.78% @ 1 MHz
1.29	242	4.35 0.29	4.34 0.42	4.32 0.33	4.30 1.01	2.55	990		4.28nF/6.65% @ 1 MHz; overcoated with PTFE
	136	2.32 0.31	2.31 0.27	2.30 0.41	2.29 1.45	2.42	-		2.27nF/10.29% @ 1 MHz
3.27	362	6.12 0.2	6.10 0.2	6.10 0.3	6.06 0.4	2.46	1820		
	236	3.74 0.2	3.73 0.2	3.72 0.3	3.70 0.7	2.30	-		
2.3	136	2.11 0.2	2.11 0.2	2.10 0.3	2.09 0.6	2.26	2850		
	385	2.22 0.23	2.21 0.28	2.20 0.39	2.19 1.16	2.1	1284		
2.3	261	1.52 0.40	1.51 0.38	1.50 0.43	1.49 1.06	2.1	1284		
	366	3.07 1.66	2.97 0.48	2.94 0.46	2.94 1.50	2.11	-		
2.3	230	2.87 1.66	2.73 1.36	2.66 1.46	2.62 2.46	(3.08)	-		
	133	-	1.32 1.66	1.29 1.06	1.28 1.56	2.57	-		
									Conducting Shorted

Table 5. Dielectric Data for Plasma Polymerized Ethylene Oxide

Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)				Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)	Comments
		100 Hz	1 kHz	10 kHz	100 kHz			
0.45	320.5	20.68nF 0.57%	20.50nF 0.68%	20.24nF 1.09%	19.90nF 3.19%	3.22		
	218	13.50 0.57	13.39 0.69	13.21 0.93	12.99 2.30	3.09		
	106	6.77 0.58	6.71 0.68	6.63 0.95	6.51 1.88	3.18		
	405	5.62 5.6	17.63 0.9	17.42 1.1	17.17 1.9	2.63		
0.535								High leakage current
								Two other devices were shorted

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Table 6. Dielectric Data for Plasma Polymerized Graft Copolymers

Structure	Thickness (μm)	Area (mm^2)	Capacitance (nF) and Dissipation Factor (%)					k	Dielectric Strength (kV/cm)	Theor. Energy Density (J/g)
			100 Hz	1 kHz	10 kHz	100 kHz				
PPVF ₂ /PPE	0.68	381	- nF - %	14.06nF 0.6%	13.94nF 1.2%	13.77nF 5.2%	2.84	1760		
		268	-	10.04 0.6	9.95 1.0	9.83 4.2	2.88	2060		
		137	-	5.45 0.6	5.40 0.8	5.33 1.8	3.06	2060		
PPE/PPVF ₂ /PPE	2.45	272	-	2.2 0.1	2.2 0.2	2.2 -	2.24	1220		
		150	-	1.2 0.2	1.2 0.2	1.19 0.4	2.21	1220		
		259	-	3.88 0.1	3.87 0.2	3.86 0.4	2.18	2470		
PPC/PPTFE/PPE	1.29	134	-	2.05 0.2	2.04 0.1	2.04 0.5	2.23	2700		
		373	6.64 0.1	6.62 0.2	6.61 0.3	-	2.55	2020		
		275	4.33 0.1	4.32 0.2	4.31 0.3	-	2.25	2050		
PPVF ₂ /PPE	1.27	123	2.22 0.2	2.21 0.2	2.21 0.3	-	2.58	2830		
		369	7.44 0.3	7.41 0.3	7.40 0.4	-	2.27	2520		
		242	4.63 0.3	4.62 0.3	4.61 0.3	-	2.16	3620		
PPTFE/PPE	1.00	141	2.75 0.3	2.74 0.3	2.73 0.4	-	2.20	3600		
		214	5.96 0.1	5.95 0.1	5.93 0.2	5.92 0.7	2.36	2680		
		112	3.12 0.2	3.11 0.2	3.10 0.3	3.09 1.3	2.36	2880		
PPE/PPTFE	0.75									

Implications about the structure of the plasma polymerized films can be drawn from these dielectric constant values. The highest values were seen with the more polar (or polarizable) starting materials, vinylidene fluoride and ethylene oxide. It appears that the orientation of the dipoles in the monomer is retained, to some extent, in the plasma polymer. Although tetrafluoroethylene contains polar fluorine atoms, the molecule is symmetrical and the dipole orientations cancel each other out. Even though the resulting plasma polymer is highly crosslinked, and thus the structure of the polymer is significantly different than the monomer, it appears that the high degree of symmetry is retained resulting in a compensation of the dipoles and a relatively low dielectric constant.

The values for the dielectric constant for PPEE and for PPTFE are higher than those published for polyethylene and polytetrafluoroethylene. Further, although the values for the dielectric strength in the plasma polymerized films were quite high, they were lower than the corresponding values for polyethylene and polytetrafluoroethylene films.

2. Thermal Stability of PPE

The thermal properties of PPE were studied by differential scanning calorimetry, DSC (Mettler TA2000B Thermal Analysis System), and by thermogravimetric analysis, TGA (DuPont 950 Thermogravimetric Analyzer interfaced with a DuPont 1090 Thermal Analyzer). DSC measures thermal transitions that occur with either an increase or decrease in heat in a material, and TGA measures thermal transitions that occur with either a gain or loss in weight.

PPE was deposited in the bell jar reactor under "normal" conditions on eight 2 in. X 2 in. glass slides. The resulting polymer was scraped off of the slides to yield 92 mg of yellow material. DSC experiments were carried out in aluminum pans under a nitrogen atmosphere. Samples were run between -100° to 500°. An exotherm was observed at ~110° to 140° which

continued, more slowly, to higher temperatures. This exothermic process could be due to thermal decomposition, coupling of residual free radicals, crosslinking, or possible chemical reaction. If the process was indeed due to radical coupling and/or crosslinking this would be a favorable process which could heal defects and therefore enhance the dielectric properties of the material. Annealing the material at 100° for 4.5 hr resulted in increasing the onset of this exothermic process to 170°. Heating the sample to 500° caused charring. The black residue, however, was not conductive, which suggests that the material was not completely decomposed, or that the structure of the residue was not graphitic. Diamond-like carbon films prepared by modified plasma polymerization techniques have been reported to be non-conducting. Direct microscopic observation during the heating of PPE on a hot stage (Mettler FP5 Hot Stage) showed no visible change in the material upon heating to 200° and then cooling rapidly to room temperature. Holding at 200° caused the material to darken in ~45 min and heating to 300° caused the sample to darken significantly, going from yellow to brown.

A plot of a TGA measurement taken in air is shown in Figure 10. There is a gain in weight between 150° and 250° suggesting that the material is being thermally oxidized. A decrease in weight starts ~245° with a transition occurring between 400° and 500°, due to thermal decomposition of the material. Decomposition below 400° may be due to the degradation of pendant groups, i.e., methyl groups, or oxygenated groups, followed by the breakdown of the polymer backbone structure. By 600° the material was essentially completely volatilized.

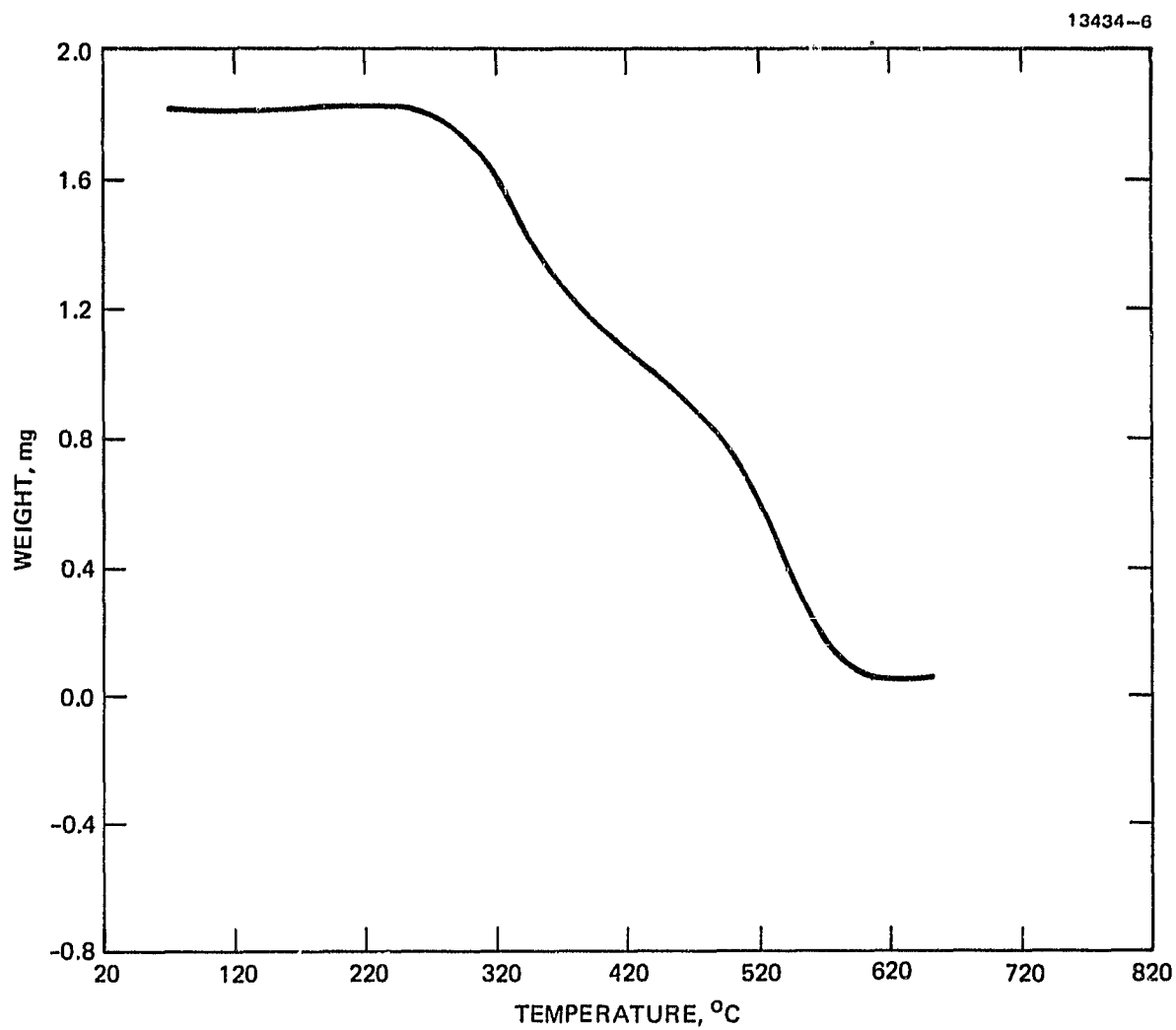


Figure 10. A plot of a TGA measurement of plasma polymerized ethane taken in air.

A similar measurement was carried out in a helium atmosphere and is shown in Figure 11. In this case there was no increase in weight at 150°, verifying that the increase under an air atmosphere was oxidation of the PPE. Weight loss commenced at ~245° and it leveled off at ~480°. The total weight loss at 600° was 58.7% of the starting weight, with a charred residue remaining.

These results show that PPE is thermally stable to 250° in the absence of oxygen. No thermal transitions attributable to glass transitions were observed. Oxidation of the material occurs at ~150°, probably at carbon-carbon double bond or residual free radical sites.

3. Residual Free Radical Reactivity

During the deposition of plasma polymerized films, residual free radicals are trapped within the matrix of the polymer. These radicals, when exposed to air, will react with oxygen to form oxygenated species both on the surface and in the bulk of the polymer. This could lead to a modification of the dielectric properties, particularly with those polymer films that are inherently nonpolar. The purpose of this study was to monitor the uptake of oxygen through the formation of carbonyl groups (C=O) which have a strong absorption in the IR. Two samples of PPE were deposited on NaCl windows and one sample of PPTFE was deposited on a KCl window. The choice of substrates was arbitrary and was dictated by our supply. No attempt was made to quench the residual free radicals. The films were monitored by Fourier Transform Infrared (FTIR) Spectroscopy for the appearance and growth of a carbonyl band around 1700 cm⁻¹. The PPE films initially showed a carbonyl absorption of about 3% which did not increase after 19 days of exposure to dry air. PPTFE showed a strong (52% absorption), broad carbonyl absorption, which is typical of PPTFE. The spectrum did not change after 7 days of exposure to dry air. Further, there was no change in the spectrum after 60 days for each of the films.

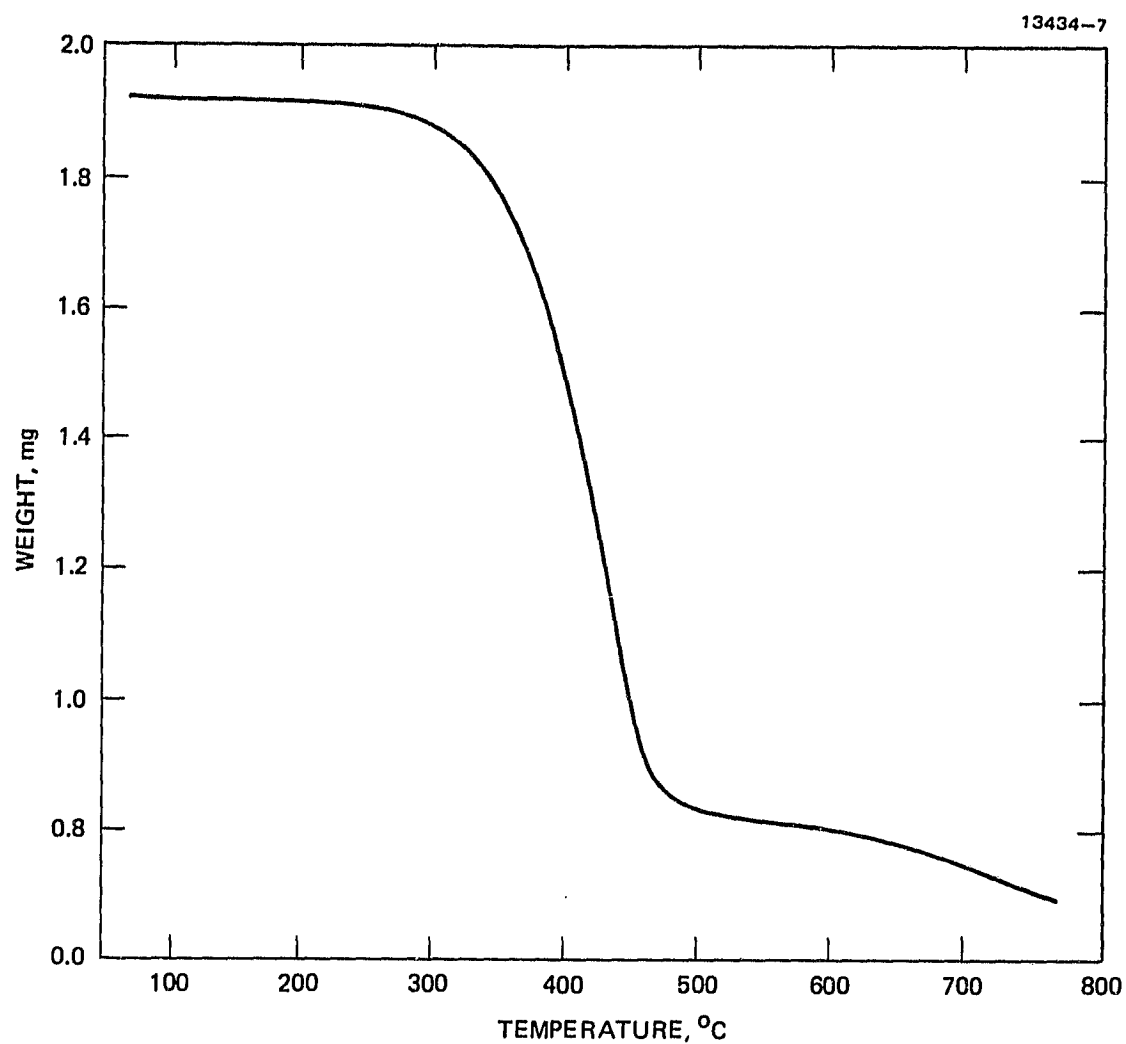


Figure 11. A plot of a TGA measurement of plasma polymerized ethane taken in helium.

Thus, PPE has a lower concentration of residual free radicals than PPTFE and it appears that, in both cases, they react with oxygen rapidly during their first exposure to air. Although it is known that the free radicals are long-lived and have been observed days following the film preparation, they appear to react more slowly after their initial exposure to air.

4. Degree of Crosslinking

Samples of PPE and PPTFE were deposited on glass microscope slides and no effort was made to quench the residual free radicals. After scraping the polymers from the slides, they were sent to Galbraith Laboratories, Inc., Knoxville, Tennessee for elemental analysis. The results of the analyses are shown in Table 7.

Table 7. Results of Elemental Analyses of PPE and PPTFE

POLYMER	%C	%H	%O	%F
PPE	85.25	10.38	1.93	0.35
	-----	-----	2.05	-----
PPTFE	33.66	-----	-----	66.50
	33.55	-----	-----	66.63

The trace of fluorine in PPE is most likely a result of traces of previously prepared fluorine-containing plasma polymerized films being sputtered during the plasma deposition of PPE. Generally, the reactor is cleaned with an oxygen plasma after each extended run. This process decomposes any organic material to volatile products (e.g., CO or CO₂) which are then pumped away. The last deposition of a fluorine-containing polymer was five months prior to the deposition of this PPE film. So although this method cleans the reactor to the point that no more volatiles are produced, it apparently is not completely effective against the last traces of fluorocarbon polymer. Another source of fluorine contamination may be the gas introduction lines. We use Teflon tubing in the gas lines and it is possible, although not too likely, that some fluorine-containing molecules may enter the ethane gas stream and be transported into the reactor. Nevertheless, the amount of fluorine in this PPE sample is small and corresponds to a C/F ratio of 386.

We derived an equation that would allow the calculation of the branch, or crosslink, density from the measured H/C ratio above. Let x be the branch density and y the measured H/C. For an uncrosslinked monomeric unit, $H/C = 2$, and for a crosslinked monomeric unit, $H/C = 3/2$. Therefore,

$$1.5x + 2(1-x) = y$$

and thus,

$$x = 4 - 2y.$$

Thus, for this PPE sample the branch density, based only on the H/C ratio, is 1.078, which points out that every monomeric unit is either crosslinked, is contained in a carbon-carbon double bond, or is a mixture of the two cases (from these data, no distinction can be made). Infrared spectroscopy data have shown that the concentration of carbon-carbon double bonds is below the detection level of the spectrophotometer and therefore the H/C ratio is a good measurement of the crosslink density. Also, these data suggest that an additional 7.8% of the monomeric units have two crosslinks.

A small amount of oxygen is present in this sample, probably through reaction of the residual free radicals with atmospheric oxygen. If the oxygen is present as R-OH, R-O-OH, R-O-O-R, or R-O-O-R' groups (where R is a polymer chain and R' is a separate polymer chain), then the H/C ratio as used above is a good representation of the branch density. However, if the oxygen is present as a carbonyl (C=O) group, then 2 hydrogen atoms are removed from the material without creating a crosslink and the calculated branch density is inadvertently high. An infrared spectrum of PPE without any prior radical quenching generally shows a small carbonyl absorption. Since the carbonyl is a strong absorption in the IR, the small absorption seen in this case implies that the concentration is very low. No well defined peaks for peroxy-type functional groups were observed, although there were broad absorptions in the spectral region where these groups absorb.

Similar calculations were made for PPTFE for the two analyses reported in Table 7. The branch densities were 1.504 and 1.492, respectively. Thus, this sample of PPTFE has a high branch density, with nearly 50% of the monomeric units having more than 1 crosslink. The oxygen concentration was not measured since accurate values cannot be obtained in the presence of significant amounts of fluorine.

D. TASK 4. REPORTING

- Provide written reports on a monthly basis describing the progress and problems encountered during the previous month.
- Provide a final report following the completion of the technical effort.

Fourteen monthly reports including a Technical Narrative, the Contractor Financial Performance Analysis Report, and the Contractor Financial Management Report, were submitted in accordance with Exhibit A and the Reports of Work sections of the contract.

Results derived from this contract work were presented at the International Union of Pure and Applied Chemistry 6th International Symposium on Plasma Chemistry, Montreal, Quebec, Canada, July 24-28, 1983. A paper was published in the Symposium Proceedings (eds. M.I. Boulos and R.J. Munz) of this meeting and is included in Appendix A of this report.

SECTION 4

CONCLUSIONS

We prepared a variety of plasma polymerized films for use as dielectric layers specifically for capacitors and demonstrated that the technique of plasma polymerization is an excellent method for the preparation of these thin films. The dielectric strength of a material is proportional quadratically to both the breakdown voltage and to the inverse of the thickness. We exploited the plasma polymerization technique, which is an excellent method for producing films with a high intrinsic voltage breakdown value on very thin films.

It was found that values of >1000 kV/cm in the dielectric strength could be obtained routinely after the proper reaction conditions for each monomer were defined. These conditions were rigorously determined for each of the five monomers studied in this program. In some cases values of >4000 kV/cm were observed. Maximization of the breakdown voltage for each device was achieved by allowing each dielectric layer to clear. Thus, high fields would form around defect points, which were generally bumps caused by either particles in the dielectric film or in the aluminum electrodes, and literally blow a hole in the device at those defects. This eliminates the buildup of high fields in the device and allows voltage to be evenly distributed across the remaining area of the dielectric film. This self-healing property was observed with all the plasma polymerized films prepared.

As seen in the various Tables of the dielectric properties of the plasma polymerized films, there was some irregularity in the dielectric strength in both the devices that were prepared from the same dielectric film, and those that were separate devices but used the same type of film. We attribute this lack of reproducibility to be a function of the aluminum used in the electrode configuration. Commonly, when a fault was observed, it was usually in the large pad of the aluminized glass devices.

We feel that this is due to either a nonuniformity of the bottom electrode or to damage incurred by the dielectric layer during the deposition of the top pad electrode. We do not believe that it is due to nonuniformity of the plasma polymerized film since we should have seen a systematic failure of devices on the other end of the slide if the nonuniformity was due to edge effects. We did not, however, make any major changes in the design of the device structures on glass slides or in the mode of deposition of the aluminum. As pointed out above, the integrity of the electrodes is an important consideration in fabricating high energy density plane capacitors. The degree of surface roughness dictates the thickness of the dielectric layer; i.e., if the surface roughness of the metal electrode is greater than the thickness of the dielectric, shorts will be present. This was demonstrated in the devices prepared on a smooth silicon substrate where capacitors using very thin PPE layers ($<3000\text{\AA}$) showed very high dielectric strengths. In fact, one of the highest values was obtained in a capacitor prepared on a silicon wafer which failed, not because of a voltage breakdown in the capacitor, but because a clearing event severed the connection between the measurement pad and the capacitor. Since this program was primarily concerned with the preparation of the dielectric layer and the measurement of its dielectric properties, we did not investigate other electrode configurations or metal layers to optimize our working capacitors. However, this consideration should not be overlooked in future studies.

We also prepared several novel graft copolymers by plasma synthesis in Task 2. The goal of this task was to increase the dielectric constant of the composite film by analogy with reported results on block copolymers. Although composite films with high dielectric strengths were obtained, the dielectric constant was not enhanced but rather seemed to be a function of the individual layers and the order in which they were deposited. In light of our results one may question the

relationship of the graft copolymers prepared under plasma conditions to the reported conventional block copolymers. In the latter case an apparently important consideration is the ability of blocks in the polymer chain to coalesce with like-blocks in an adjacent chain at elevated temperature to form a phase separated system. Although the deposition of plasma polymerized graft copolymers would yield a phase separated system, each constituent layer is highly crosslinked and therefore not mobile. Thus, it appears that the plasma polymerized graft copolymers comprising polar and nonpolar films do not mimic the phase separated properties of those of elevated-temperature block copolymers.

The capacitance, dissipation factor, and breakdown voltage were measured for five different plasma polymerized films and a number of plasma polymerized graft copolymer films. The capacitance was found to be nearly insensitive to increasing frequency, but the dissipation factor increased rapidly at frequencies above 10 kHz. This results from the high crosslink density in the film which holds the dipoles in a fairly rigid configuration within the amorphous matrix. Thus, the dipoles are unable to realign with increasing frequency. Breakdown voltage measurements led to calculations of the dielectric strength which were generally >1000 kV/cm, and as high as >4000 kV/cm in some cases, as discussed above. We were unable to achieve a theoretical energy density goal of 5 J/gm in any of the devices tested. However, we feel that films prepared by plasma polymerization have the capability of handling an energy density of that value when they are incorporated into capacitors of the proper design, i.e., by using very thin layers over extremely smooth electrode surfaces. The demonstration of the high dielectric strengths in this program suggests that this theoretical energy density goal is achievable under the proper sets of testing conditions.

We found that PPE had very good thermal stability, particularly in the absence of oxygen. TGA measurements showed that PPE in the presence of oxygen began to thermally decompose at $\sim 150^\circ$, whereas in the absence of oxygen this temperature was nearly 250° . No glass transition for PPE was observed due to the highly crosslinked structure of this material.

The reaction of residual free radicals that were trapped within the polymer matrix of PPE and PPTFE was observed by the appearance of a carbonyl group in the FTIR spectra of these materials. It was seen that the free radicals reacted rapidly with oxygen upon their initial exposure to air. Further exposure to air over 60 days did not appreciably increase the initial carbonyl absorption.

We have demonstrated that the technique of plasma polymerization is an excellent one for the preparation of thin films to be used as high energy dielectric layers for capacitors. Very thin films from monomers with varied structures can be prepared with high breakdown voltage values which lead to high dielectric strengths.

Although this program was intended to be an applied research project to develop plasma polymerized films as dielectric layers for high energy density capacitors, a significant amount of data was gathered that alludes to some of the fundamental aspects of dielectric breakdown in these materials. Plasma polymerized films possess a high enough Young's modulus due to their crosslinked structure so that electromechanical breakdown (e.g., squeezing of the material due to a compressive force on the sample by mutual coulombic attraction of the electrodes as the voltage is applied) was not observed. Internal gas discharges are the main cause of breakdown in conventional polymeric dielectrics because of voids that are left in the material during film-forming processes. The manifestation of these types of discharges is the propagation of tree-like growth of dendritic erosion channels from the void toward the electrodes. We did not observe breakdown mechanisms

of this type; the method of deposition of the dielectric in plasma polymerization precludes the formation of voids since the process is carried out under vacuum and the growth of the film is continuous. The process also eliminates the absorption of dirt or moisture at the surface which can lead to tracking and ultimate breakdown.

REFERENCES

1. J. Goodman, J. Polym. Sci., 44, 551 (1960).
2. L.V. Gregor, IBM J. Res. Develop., 12, 140 (1968), and references cited therein.
3. A. Bradley, and J.P. Hammes, J. Electrochem. Soc., 110, 15 (1963).
4. M. Stuart, Proc. IEE, 112, 1614 (1965); M. Stuart, Nature, 199, 59 (1963).
5. C. Sar, M. Valentin, and B. Ai, J. Appl. Polym. Sci., 24, 503 (1979).
6. J.M. Tibbitt, A.T. Bell, and M. Shen, J. Macromol. Sci., Chem., A10, 519 (1976).
7. R. Behn, H. Hagedorn, J. Kammermaier, M. Kobale, H. Pachonik, D. Ristow, and G. Seebacher, Bundesminist. Forsch. Technol., Forschungsber., Technol. Forsch. Entwickl., BMFT-FB T 76-66 (1976)
8. G. Smolinsky and J.H. Heiss, Amer. Chem. Soc., Div. Org. Coatings Plast. Chem., Pap. 28, 537 (1968).
9. J.M. Pochan and R.G. Crystal, "Dielectric Properties of Polymers," ed. F.E. Karasz, Plenum Press, New York, N.Y., p. 313 (1970); J.M. Pochan, Polym. Preprints, 12, No. 1, 212 (1971).

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APPENDIX A

PLASMA POLYMERIZED HIGH ENERGY

DENSITY DIELECTRIC FILMS

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ABSTRACT

We demonstrated that plasma polymerization is an excellent method for the preparation of high energy density dielectrics. The technique enhances quadratically the energy density of the dielectric by allowing for the deposition of very thin films while retaining a high intrinsic breakdown voltage of the polymer due to its uniformity and pinhole-free structure.

1. INTRODUCTION

The use of polymer thin films as dielectric materials corresponds nearly to the emergence of polymer chemistry as a branch of science. However, it was not until 1960 when Goodman¹ developed a useful preparation technique that plasma polymerized films could be studied² for this purpose. Since that time, several research groups² have investigated the dielectric properties of polymers prepared in a glow discharge.

The principal advantage of plasma polymerized films is that they can be prepared as very thin, pinhole-free, integral coatings. They are known to have a high dielectric strength, which coupled with the small thickness of the film, enhances quadratically the energy capacity of the material.

Bradley and Hammes³ measured the conductivity of plasma polymerized films derived from 40 monomers varying in structure and polarity. The majority of these films¹ had conductivities in the range of 10^{-16} to 10^{-14} (ohm-cm) at 150°C. Stuart⁴ reported on the dielectric properties of plasma polymerized styrene, which was deposited on a continuous roll of aluminum foil. He found a dielectric loss factor ($\tan \delta$) of 0.001 to 0.003 at 1 kHz and 20°C, with a permittivity of 2.6 to 2.7 between 10^2 and 10^5 Hz. Sar, et al.⁵ showed later that the addition of an antioxidant (catechol) to the styrene prior to deposition prevented the formation of polar OH and CO groups in the polymer, and decreased the dielectric loss by a factor of 4-5. Tibbitt, et al.⁶ reported similar results with plasma polymerized ethylene-acetylene, ethane-vinyl chloride and tetrafluoroethylene.

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Another example of continuous deposition of plasma polymerized films derived from cyclohexane and perfluorocyclobutane was reported by Behn et al. These films had a dielectric strength of 8×10^6 V/cm. Self-healing wound capacitors of consistently high quality were fabricated from the metallized carrier foils covered with the dielectric film.

Smolinsky and Heiss⁸ demonstrated the reproducibility of the technique for the preparation of capacitors. Out of nearly 200 capacitors, they were able to obtain an 86% yield of working devices. Some shorted capacitors were cleared of defects by subjecting them to a 20V capacitance discharge.

Often, the failure of conventional polymers used in capacitors can be traced to impurities trapped within the polymer matrix and physical defects arising from handling during the preparation of the device. The magnitude of these effects is reduced tremendously by preparing the dielectric as a thin film in a plasma since the process uses pure monomers and is carried out under vacuum conditions. The dielectric film need not be handled once it is deposited.

In this paper, we report the preparation of "device precursors" and capacitors assembled with aluminum film-electrodes on glass slides using submicrometer thicknesses of a variety of films and graft copolymers prepared by plasma polymerization. A particular goal of this research program was to enhance the energy density, k_c (energy per unit mass), of the dielectric material. The quantity k_c can be expressed as:

$$k_c \equiv \frac{E}{m} = \frac{\kappa \epsilon_0}{2 \rho} \left(\frac{V}{d} \right)^2$$

where E is the energy stored, m is the mass, κ is the relative permittivity of the dielectric, ϵ_0 is the permittivity of free space (8.85×10^{-14} F/cm), ρ is the density of the dielectric (g/cm^3), V is the breakdown voltage, and d is the thickness of the dielectric film. Thus, for a given device, the energy density stored increases with voltage across the leads in a quadratic fashion with the limit being determined in principle by the ultimate breakdown voltage of the dielectric. Furthermore, the energy storage density also depends quadratically on the reciprocal of the film thickness. The method of plasma polymerization offers advantages over bulk polymerization through improvements in the quality of the film and elimination of the dangerous material processing steps.

2. EXPERIMENTAL

Plasma polymerized films were prepared from both polar and nonpolar monomers. The specific gases used in this study were ethane, ethylene, tetrafluoroethylene, vinylidene fluoride, and ethylene oxide. They were used as received without any further purification. The deposition of the polymers was carried out in parallel plate, capacitively coupled reactors equipped with a mechanical pump and pressure controllers. General reaction

conditions consisted of a monomer flow rate of ~ 10 ml/min @ STP at a reaction pressure of ~ 1 Torr. The plasma was struck using an rf generator (13.56 MHz) at 200-300 W through an impedance matching network. Since the deposition rate was calibrated under particular conditions for a given monomer, desired thicknesses could be obtained by running the experiment for a predetermined time.

Device precursors were prepared by depositing the plasma polymerized film on a thin aluminum film, which had been deposited on a glass microscope slide. Capacitors were assembled from these device precursors by evaporating aluminum pads of different areas onto the dielectric layer. Figure 1 illustrates the configuration of these devices.

Figure 2 shows the schematic of the circuit used to measure the dielectric properties of the plasma polymerized films. A $0.091 \mu\text{F}$ mica capacitor, which was charged to 10V, was discharged into each test capacitor to facilitate the clearing. The capacitance (from which the dielectric constant was calculated) and dissipation factor were measured at 100 Hz, 1 kHz, 10 kHz, and 100 kHz. The breakdown voltage measurements were then made. Initially, as the voltage was increased, the capacitor would momentarily break down, clearing at defect points in the device. From that time on, it would not break down at that voltage or any lower voltage. The breakdown process appeared to blast away the aluminum and plasma film from the area around the weak point such that high fields could no longer concentrate at the defect. We estimate that these clearing events did not remove more than 2% of the active area of the capacitor.

3. RESULTS AND DISCUSSION

The largest effort to prepare films as high energy dielectrics for capacitors was directed towards the development of plasma polymerized ethane (PPE) for this purpose. For samples between 1- to 2- μm thick, dielectric strengths of greater than 1000 kV/cm were commonly observed. Thicknesses of between 0.6 and 0.8 μm yielded reproducible dielectric strengths of over 4000 kV/cm. Film thicknesses of less than 0.5 μm did yield working capacitors but with nonreproducible results depending upon the surface roughness of the aluminum film substrate. However, reproducible results were obtained using a highly polished silicon substrate instead of a glass slide. In this case, a 0.28 μm -thick PPE film showed a dielectric strength of over 4000 kV/cm. These results amplify the need for considering all aspects in fabricating planar capacitors, rather than just the dielectric film. This is particularly true when trying to increase the dielectric strength by reducing the thickness of the dielectric film.

Reaction conditions were established to give uniform plasma polymerized ethylene (PPEE) films with a deposition rate of 0.45 $\mu\text{m/hr}$. As with PPE, high dielectric strengths were obtained with values of greater than 2000 kV/cm being commonly observed. A 0.46 μm -thick PPEE film yielded a working capacitor with a dielectric strength of 2170 kV/cm.

We found that the preparation of plasma polymerized vinylidene fluoride (PPVF₂) was more difficult than originally anticipated. The monomer would spontaneously polymerize in the reactor, even before a plasma was struck, yielding a polymeric powder. Our technique was adjusted to minimize this problem by thoroughly evacuating the system before the introduction of the vinylidene fluoride and then striking the plasma as soon as the system equilibrated to a constant pressure after the introduction of the monomer gas. We also found that the aluminum electrodes had to be cleaned with Micro Cleaner, thoroughly rinsed with deionized water, dried, and scrubbed with an oxygen plasma prior to the deposition of the PPVF₂ to allow for good adhesion of the polymer film. If this procedure was not carried out, the film, although initially very uniform, readily crazed with the slightest provocation.

Films of plasma polymerized tetrafluoroethylene (PPTFE), prepared in one reactor, appeared to be highly uniform but showed significant leakage current. This resulted in little reproducibility in the capacitance measurements and therefore in the dielectric constant calculations. However, PPTFE films prepared in another reactor did not show this conduction and dielectric data could be readily obtained. These results suggest that the reaction conditions in the first reactor were not completely optimized for the best dielectric film, even though they were of excellent appearance. Dielectric strengths of more than 1000 kV/cm up to 2400 kV/cm were obtained with these films. Film thicknesses of about 0.5 μ m were adequate to cover surface defects on aluminized glass slides and reproducible data could be obtained without having to force clearing events to occur.

Our initial attempts to prepare plasma polymerized ethylene oxide (PPEO) films were hampered by the fact that the ethylene oxide reacted with the Viton o-rings seals in the rotameters. This resulted in a non-uniform flow into the reactor and subsequently poor quality films. Replacement of the seals with Teflon alleviated the problem. It was found that a 0.45 μ m-thick film of PPEO yielded working capacitors with dielectric strengths approaching 2000 kV/cm.

We also prepared, by plasma synthesis, graft copolymers comprising layers of nonpolar hydrocarbon polymers and polar or polarizable polymers derived from vinylidene fluoride, and tetrafluoroethylene. The residual free radicals of the first deposited layer interacted with the active species involved in the formation of the second layer to form carbon-carbon bonds. This formed a system with a well defined nonpolar-polar interface, and each layer of the system could interact continuously. It was reported⁹ that block copolymers comprised of polystyrene and poly(ethylene oxide) showed unusually high dielectric constants caused by phase separation of the two blocks at elevated temperatures. By analogy, we expected that enhanced dielectric constants in these graft copolymers may be obtained. The structures PPE on PPVF₂, PPE on PPTFE, and PPTFE on PPE were prepared. Although the graft copolymers showed high dielectric strengths approaching 4000 kV/cm, the dielectric constants of the structures were not enhanced over the values of the individual layers. Although the deposition

of plasma polymerized graft copolymers would yield a phase separated system, each constituent layer is highly crosslinked and therefore not mobile. Thus, it appears that these plasma polymerized graft copolymers do not mimic the phase separated properties of the elevated-temperature linear block copolymers.

High dielectric strengths were observed with all materials studied. Thus, this property appears to be a function of the plasma polymerization technique rather than being an inherent property of each particular starting material. In general, the higher values of the dielectric strength were observed in the devices using thin dielectric films. The capacitance does not appear to be a function of frequency, within the frequency range of 10^2 - 10^5 Hz, but the dielectric loss (dissipation factor) is indeed influenced by frequency. The dissipation factor was generally much below 1% at frequencies below 10 kHz but increased significantly at frequencies above 10 kHz.

The dielectric constants, however, are a function of the structure of the starting materials, and consequently, of the resulting plasma polymerized film as shown in Table 1. Implications about the structure of the plasma polymerized films can be drawn from these dielectric constant values. The highest values were seen with the more polar (or polarizable) starting materials, vinylidene fluoride and ethylene oxide. It appears that the orientation of the dipoles in the monomer is retained, to some extent, in the plasma polymer. Although tetrafluoroethylene contains polar fluorine atoms, the molecule is symmetrical and the dipole orientations compensate each other. Even though the resulting plasma polymer is highly crosslinked, and thus the structure of the polymer is significantly different from that of linear polytetrafluoroethylene, it appears that the compensation of the dipoles is essentially retained, and the product has a relatively low dielectric constant.

ACKNOWLEDGEMENT

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REFERENCES

- (1) Goodman, J., J. Polym. Sci., 44, 551 (1960).
- (2) Gregor, L.V., IBM J. Res. Develop., 12, 140 (1968), and references cited therein.
- (3) Bradley, A. and Hammes, J.P., J. Electrochem. Soc., 110, 15 (1963).
- (4) Stuart, M., Proc. IEE, 112, 1614 (1965); Stuart, M., Nature, 199, 59 (1963).
- (5) Sar, C., Valentin, M., and Ai, B., J. Appl. Polym. Sci., 24, 503 (1979).
- (6) Tibbitt, J.M., Bell, A.T., and Shen, M., J. Macromol. Sci., Chem., A10, 519 (1976).

- (7) Behn, R., Hagedorn, H., Kammermaier, J., Kobale, M., Pachonik, H., Ristow, D., and Seebacher, G., Bundesminist. Forsch. Technol., Forschungsber., Technol. Forsch. Entwickl., BMFT-FB T 76-66 (1976).
- (8) Smolinsky, G., and Heiss, J.H., Amer. Chem. Soc., Div. Org. Coatings Plast. Chem., Pap. 28, 537 (1968).
- (9) Pochan, J.M. and Crystal, R.G., "Dielectric Properties of Polymers," ed. Karasz, F.E., Plenum Press, New York, N.Y., p. 313 (1970); Pochan, J.M., Polym. Preprints, 12, No. 1, 212 (1971).

Table 1. Mean measured dielectric constants.

POLYMER	MEAN DIELECTRIC CONSTANT, k	STANDARD DEVIATION
PPE	2.50	0.25
PPEE	2.75	0.26
PPVF ₂	3.16	0.41
PPTFE	2.39	0.16
PPEO	3.03	0.27

ORIGINAL SCHEMATIC
OF POOR QUALITY

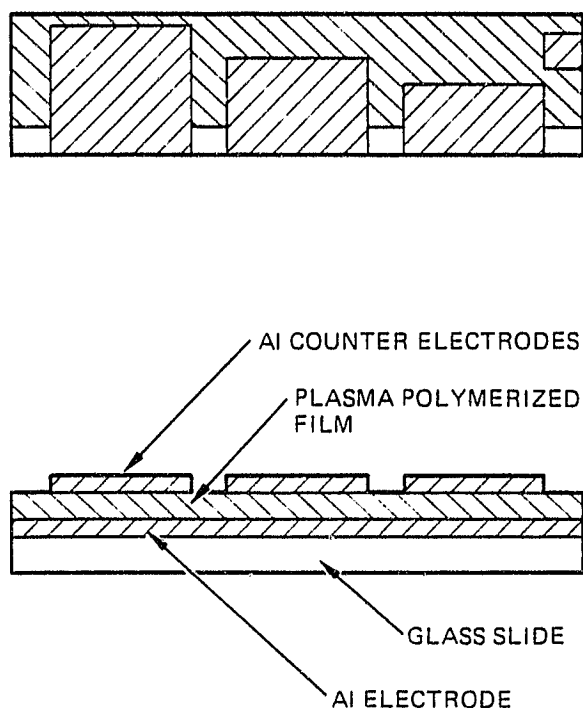


Figure 1. Test capacitors on aluminized glass slides.

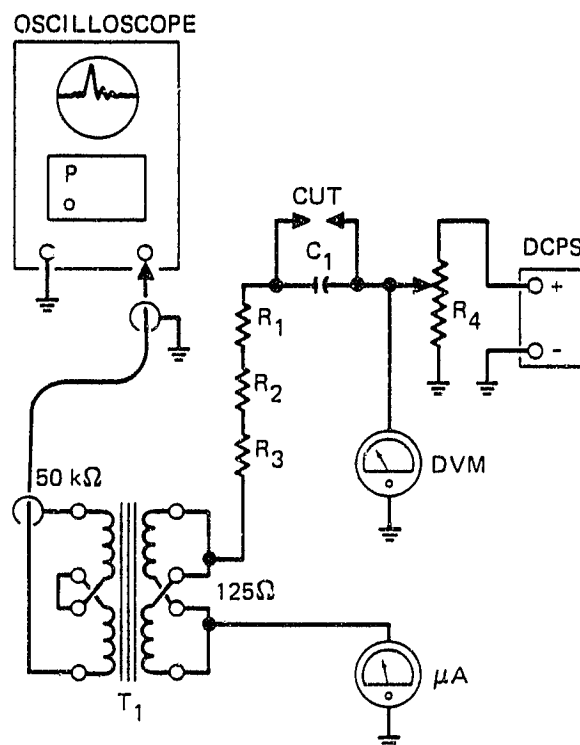


Figure 2. Schematic of the breakdown voltage measurement circuit.